

NASA TECHNICAL MEMORANDUM

NASA TM-77673

DETERMINATION OF THE VISCOSITY NUMBER OF THERMOPLASTICS
IN DILUTE SOLUTION; POLYAMIDES (PA)

German Institute of Standards (DIN)

Translation of "Bestimmung der Viskositätszahl von Thermo-
plasten in verdünnter Lösung", DIN (German Institute of
Standards) Standard No. 53 727, Plastics Standards Committee
of the DIN, Berlin, West Germany, January 1980, pp. 1-4

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 SEPTEMBER 1985

1. Report No. NASA TM-77673	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle DETERMINATION OF THE VISCOSITY NUMBER OF THERMO- PLASTICS IN DILUTE SOLUTION; POLYAMIDES (PA)		5. Report Date SEPTEMBER 1985	6. Performing Organization Code
7. Author(s) DIN (Deutsche Institut fuer Normung - German Institute of Standards)		8. Performing Organization Report No.	10. Work Unit No.
9. Performing Organization Name and Address RMS Associates P.O. Box 8757, BWI Airport, MD 21240		11. Contract or Grant No. NASW-4070	13. Type of Report and Period Covered TRANSLATION
12. Sponsoring Agency Name and Address NATIONAL AERONAUTICS AND SPACE ADMINISTRATION WASHINGTON, D.C. 20546		14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Bestimmung der Viskositätszahl von Thermoplasten in verdünnter Lösung", DIN (German Institute of Standards) Standard No. 53 727, Plastics Standards Committee of the DIN, Berlin, West Germany, January 1980, pp. 1-4			
16. Abstract This West German Standard presents a test used to determine the vis- cosity number of polyamides and copolyamides which are easily diluted in sulfuric acid, and for other polyamides which are less easily diluted in sulfuric acid, and which are diluted in m-cresol. As formic acid is often used in industry instead of sulfuric acid, this solvent is also presented as an alternative, however sulfuric acid is preferred because of the thermodynamic solubility characteristics of the polyamides and the handling safety. In addition, it is shown which solvent should be used for each polyamide. Finally, determinations concerning the pre- paration of the samples are presented. Using the viscosity number, a determination of the molar mass of the polyamides is possible.			
17. Key Words (Selected by Author(s))		18. Distribution Statement Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 13	22. Price

Plastics Standards Committee (FNK), of the
German Institute of Standards, Reg. Assn.
DIN Standards Committee for Material Testing

Testing of Plastics

Determination of the Viscosity Number of Thermoplastics in
Dilute Solution; Polyamides (PA)

(Previous editions: 04.63, 11.67, 06.71)

1. Purpose and application

This test is used to determine the viscosity number of PA 6, PA 66, PA 69, PA 610, PA 612, PA 6-3-T, copolyamides and other polyamides easily diluted in sulfuric acid, as well as for PA 11, PA 12 and other polyamides which are less easily diluted in sulfuric acid, and which are diluted in m-cresol.

As formic acid is often used in industry instead of sulfuric acid, this solvent will also be presented as an alternative.

The kinematic viscosity of the solvents and the solutions containing 0.5 g of polyamide per 100 cm³ were measured at (25 plus or minus 0.1) degrees centigrade.

Cast polyamides, such as PA 6G [1] and PA 12 G, which are manufactured according to the method using activated anionic polymerization of lactamine, are normally not soluble in the solvents indicated under the conditions of this standard.

Using the viscosity number, a determination of the molar mass of the polyamides is possible.

2. Associated Standards

DIN EN 60

Glass fiber reinforced plastics;

	determination of the annealing loss
DIN 51562, Section 1	Viscosity; measurement of the kinematic viscosity using the Ubbelohde viscosimeter; normal model
DIN 53 738	Testing of plastics; determination of the extractible component content

3. Concept

The viscosity number J in cm³ per gram is the quotient of the kinematic viscosity of the solution and the solvent, divided by the mass concentration of PA in the solution:

$$J = \left(\frac{v}{v_0} - 1 \right) \cdot \frac{1}{\rho(PA)}$$

in which the following definitions apply:

- V kinematic viscosity of the solution in mm² X s⁻¹
- V₀ kinematic viscosity of the solvent in mm² X s⁻¹
- Q (PA) mass concentration of polyamide in the solution
 in grams per cm³.

Note: The kinematic viscosities may be replaced by the flow times as long as the same viscosimeter is used (see section 9).

4. Designation of the Method

The designation of the method of determining the viscosity number using the method A (A) of the extraction of the extractible components of polyamides (PA) in dilute solutions is:

Viscosity number DIN 53 727-A-PA

5. Test Equipment and Substances [2]

5.1 Test equipment

- Ubbelohde viscosimeter
 - No. II (inner diameter of the capillaries: 1.13 mm) when using sulfuric acid or m-cresol as the solvent, and
 - No. I (inner diameter of the capillaries: 0.63 mm) when using formic acid as the solvent
- in accordance with DIN 51 562, Section 1

- Stopwatch with a scale division of 0.1 seconds
- 50 ml or 100 ml graduated flask with polished conical sleeve and stopper; for example, see DIN 12 664 (calibrated at a reference temperature of 20 degrees centigrade)
- Shaking or magnetic stirring equipment
- Warming chamber; for example see DIN 50 001, Section 1, for temperatures between 40 and 100 degrees centigrade
- Vacuum drying chamber
- Glass filter crucible with a maximum pore width of 1.0 to 90 cubic micrometers [3]
- or
- Laboratory centrifuge with 3000 min⁻¹ RPM
- Clear water bath thermostat for a temperature of 25.0 degrees centigrade, plus or minus 0.05 degrees
- Water bath thermostat for a temperature of 20 degrees centigrade, plus or minus 0.1 degree
- Scale with a permissible variation of 1 or 2 micrograms

5.2 Test substances

Solvents:

- a) Sulfuric acid with a mass content of 96%, plus or minus 0.15%
 Determining factor for the kinematic viscosity:
 10.8mm² X s⁻¹

[1] G = cast

[2] The Plastics Standards Committee (FNK), Burggrafenstrasse 4-10, 1000 Berlin 30, will provide information concerning sources of supply.

[3] Glass filter crucible G2, G3, G4 or G5.

/page 2 DIN 53 727/

Use for: PA 6, PA 66, PA 69, PA 610, PA 612, PA 6-3-T
and copolyamides

- b) Formic acid with a mass content of 90%, plus or minus 0.15%.
Determining factor for the kinematic viscosity: $1.35 \text{ mm}^2 \text{ X s}^{-1}$.
Use for: PA 6, PA 66, PA 69, PA 610 and copolyamides

Note 1: The amounts of sulfuric acid and formic acid given
must be strictly maintained.

Note 2: Preferably, sulfuric acid should be used.

- c) m-cresol, distilled at a pressure of approximately. 4 mbar.
Pressure equilization is carried out using nitrogen in
order to avoid oxidation; it should be kept in the dark in
brown bottles.

Requirements:

Before use, the m-cresol should be clear and colorless.

Mass content of m-cresol.....min. 99%

Mass content of o-cresol.....max. 0.3%

Mass content of water.....max. 0.13%

Note: Determination of these contents is done using
gas chromatography.

Determining factor for the kinematic viscosity:
 $13.0 \text{ mm}^2 \text{ X s}^{-1}$

Use for: PA 11, PA 12 and for the polyamides indicated
for sulfuric acid.

Note: The viscosity numbers obtained from a sample may
significantly differ from each other when using different
solvents. Therefore, the viscosity numbers of a sample increase
when they are diluted in the solvents given, in the following
order: formic acid, sulfuric acid and m-cresol. The increase
for the polyamides PA 610, PA 612 PA 11 and PA 12 is especially
significant.

In certain cases it may become necessary to use another solvent
or solvent mixture in place of sulfuric acid, m-cresol or formic
acid. This procedure should be agreed to and mentioned in the
test report.

Cleaning agents:

- Chromosulfuric acid (concentrated sulfuric acid, saturated with potassium dichromate)

When working with chromosulfuric acid, the safety regulations contained in the pertinent notices of the chemical industry professional association must be taken into consideration.

- Chemically pure acetone.

6. Sample Selection

An average sample of the product to be tested should be taken, and pulverized when necessary (see DIN 53 733).

7. Number of Measurements

At least two measurements per sample must be made.

8. Preparation of the Sample

8.1 General

If the sample to be tested contains other materials, then the following procedure must be followed:

- a) For a mass content of more than 2% (or in questionable cases, 1%) of extractible components, i.e., softeners or caprolactam, one of the extractions stated in section 8.3 must be carried out.
- b) For a mass content of more than 0.5% of glass fibers, glass spheres or other fillers, the annealing loss should be determined quantitatively according to section 8.4, and the weight of sample should be corrected accordingly.

Should the polyamides contain other polymers, such as polyolefins or admixtures for combustion protection, special procedures for their determination must be agreed upon, and the weight of sample corrected accordingly.

8.2 Drying

The mass content of water in the sample may not exceed 0.5%. If the water content is unknown, the pulverized sample should be dried in a vacuum drying chamber for approximately 16 hours at a pressure of approximately 20 mbar and a temperature of approximately 80 degrees centigrade.

8.3 Extraction of Extractible Components

8.3.1 Method A

The extraction of the extractible components is carried out according to DIN 53 738 with a sample amount weighing approximately 1.5 g. Methanol is used as the extraction liquid. A Twisselmann extractor (heat extraction) is preferably used as the extraction vessel. The extraction time should be from 5 to 10 hours.

For copolyamides which are soluble in methanol, monomer components may also be extracted according to DIN 53 738, however methylene chloride should be used as the solvent.

8.3.2 Method B

The sample is heated twice with reflux, each for approximately 6 hours in 50 to 100 cm³ of methanol, where the methanol is changed after the first heating.

8.3.3 Drying after extraction

After extraction according to methods A or B, the sample is dried in a warming chamber for at least 3 hours at from 45 to 65 degrees centigrade. Then, no correction to the weight of sample will be necessary to determine the viscosity as long as no additional unsoluble admixtures are present.

8.4 Determining the Insoluble Components Such as Glass Fibers and Other Non-Soluble Fillers to Determine the Weight of the Sample

8.4.1 Implementation

The mass content of glass fibers and other non-volatile inorganic fillers, such as mineral materials for example, in the sample is obtained by determining the annealing loss according to DIN EN 60.

8.4.2 Calculating the weight of sample

The mass of the corrected weight of sample m_1 in grams is calculated according to the following equation:

$$m_k = \frac{m}{1 - \frac{\omega}{100}}$$

in which the following definitions apply:

m required mass of pure polyamide in the weight of sample in g.

w mass content of unsoluble components in the polyamide in %.

9. Implementation

9.1 Cleaning of the viscosimeter

The Ubbelohde viscosimeter should be cleaned with chromosulfuric acid before the first use and from time to time during use. Finally, it should be rinsed with distilled water and acetone, and dried with air free of dust and oil.

Between two successive tests, the viscosimeter should be rinsed several times with the solvent and then with acetone, then dried as previously described.

9.2 Producing the solution

From the sample,

250 mg (with an accuracy of 1 mg) is weighed into a 50 ml graduated flask, or

500 mg (with an accuracy of 2 mg) is weighed into a 100 ml graduated flask,

after which approximately 40 ml, or 80 ml, of the solution is added. For polyamides with admixtures, the weight of sample must be corrected accordingly (see Section 8.4). Then, the graduated flask is sealed and the sample is dissolved at room temperature in the solution using either 5-10 hours of shaking in a shaking apparatus, or by stirring in a magnetic stirring apparatus.

When being dissolved in m-cresol, the solution temperature may be up to 80 degrees centigrade.

After cooling the solution to 20 degrees centigrade, plus or minus 0.1 degree, the graduated flask is filled with solvent to the measuring mark and the solution is well mixed by shaking.

If the sample contains admixtures which give off gasses in sulfuric acid, i.e., carbon dioxide from samples containing chalk, m-cresol should be used as the solvent.

The sample should be completely dissolved after shaking or stirring. For PA substances without admixtures the solution will be clear.

Note: For highly molecular polyamides, streaking can not be avoided even with extended shaking or stirring. The results of such measurements are only suitable for the relative comparison of similar samples.

If formic acid is used as the solvent, its volatility may cause incorrect results when used in automatic equipment.

9.3 Separation of glass fibers and coarse granular admixtures from the solution

Glass fibers or coarse granular admixtures, which obstruct the flow of the solution through the capillaries, must be separated.

For this purpose, the solution is filtered through a suitable glass filter crucible (see Section 5.1) with a maximum pore width between 1.0 and 90 micrometers, or centrifuged at approximately 3000 min⁻¹ RPM.

For some sample solutions, such as glass fiber reinforced polyamides, the clear solution may be decanted or measured directly 4-8 hours after the fibers or fillers have settled, without additional filtering or centrifuging.

9.4 Measuring the flow times of the solution and the solvent

The measurement of the flow times of the solution and the solvent is carried out with the same viscosimeter according to DIN 51 562, Section 1 (December 1978 edition), paragraph 9, at 25 degrees centigrade, plus or minus 0.05 degrees.

The flow time of each liquid is measured exactly to within 0.1 second three times in a row.

The variation in the flow times obtained for each liquid may be:

max. 0.4 seconds for viscosity numbers under 260 cm³ per gram;

and,

max. 1 second for viscosity numbers above 260 cm³ per gram.

10. Evaluation

According to this standard, the viscosity number J in cm³ per gram is calculated according to the following equation:

$$J = \left(\frac{t}{t_0} - 1 \right) \cdot \frac{1}{\rho(\text{PA})}$$

in which the following definitions apply:

t arithmetic mean of the flow times of the solution;

to arithmetic mean of the flow times of the solvent;

Q(PA) mass concentration of polyamide in the solution in grams per cm³.

Comparability [4] of the results: less than plus or minus 3%

Repeatability [4] of the results: less than plus or minus 1.5%

(When using sulfuric acid as the solvent)

Note: When using formic acid as the solvent and the Ubbelohde viscosimeter No. 1, the flow times t_0 and t must be corrected according to the Hagenbach tables of the viscosimeter manufacturer. Various time corrections dependent upon the flow time are used according to the shape of the capillaries of the viscosimeter (transition from the lower end to the inverted level), which can be obtained from the operating instructions of the viscosimeter used.

11. Test Report

Based on this standard, the following must be indicated in the test report:

- Type and designation of the polyamide tested
- if necessary, type and content of unsoluble components
- determination methods
- extraction methods
- if necessary, drying conditions
- weight of sample m_k or m
- solvent used
- Ubbelohde viscosimeter used, according to DIN 61 562, Section 1
- flow time of the solution in seconds
 - individual values
 - mean values
- flow time of the solvent in seconds
 - individual values
 - mean values
- viscosity number rounded to a whole number

- conditions agreed upon which do not conform to this standard
- test data

[4] See DIN 51 848, Section 1

Explanation

The present standard was established by the 303.4 "Polyamide Substance" Sub-committee.

Aside from re-editing of the text, the following changes to the June 1971 edition were made:

In addition to the solvent m-cresol, in this standard sulfuric acid and formic acid were indicated as solvents. Sulfuric acid is preferred because of the thermodynamic solubility characteristics of the polyamides and the handling safety. In addition, it is shown which solvent should be used for each polyamide. Finally, determinations concerning the preparation of the samples is presented. The determinations in this standard conform only partially with the ISO Standard ISO 307-1977, "Plastics; determination of viscosity number of polyamides in dilute solution". In the ISO standard, only formic acid and m-cresol are given as solvents; also, this does not make any determination concerning the use of particular solvents for each polyamide nor, is the preparation of the sample presented.